Fires and Explosions

Plant Hazards

- Chemical hazards: flammability, reactivity, toxicity
- Plant incidents: fires, explosions, toxic releases, Tab 1-6. p 15.
- Fires: combustibility of materials
- Explosions: initiation, propagation, damage potential
- Reduction of fire and explosion hazards

Fire Triangle

- Required for combustion: fuel, oxygen, ignition source or oxidizer
- Source of ignition can be internal to fuel
- Prevention: based primarily on avoiding flammable mixtures with air
- Explosions differ from fires: rate of combustion

Liquid Flash Point (FP)

- ♣ FP: Lowest temperature at which a vapor pressure exists for an ignitable mixture with air.
- FPs are known for most pure liquids but only for a few mixtures of flammable components
- ♣ FP for mixtures with 1 flammable specie: determine temperature for the vp of the flammable in the mixture to equal the pure vp at its FP.
- **FP** for mixtures with > 1 flammable: measure

Flammability Limits for Gases

- Flammability region for each gas bounded by LFL and UFL
- Most flammability data are for pure gases
- Flammability data for gas mixtures can be measured in a flash point apparatus
- ♣ Estimate LFL and UFL using the Le Chatelier model that assumes non-interacting species: Not accurate for polar species or high P.

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} \qquad UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}}$$

10/15/2011 l-1 L-1 L-1 L-1 2010 Fall l-1 L

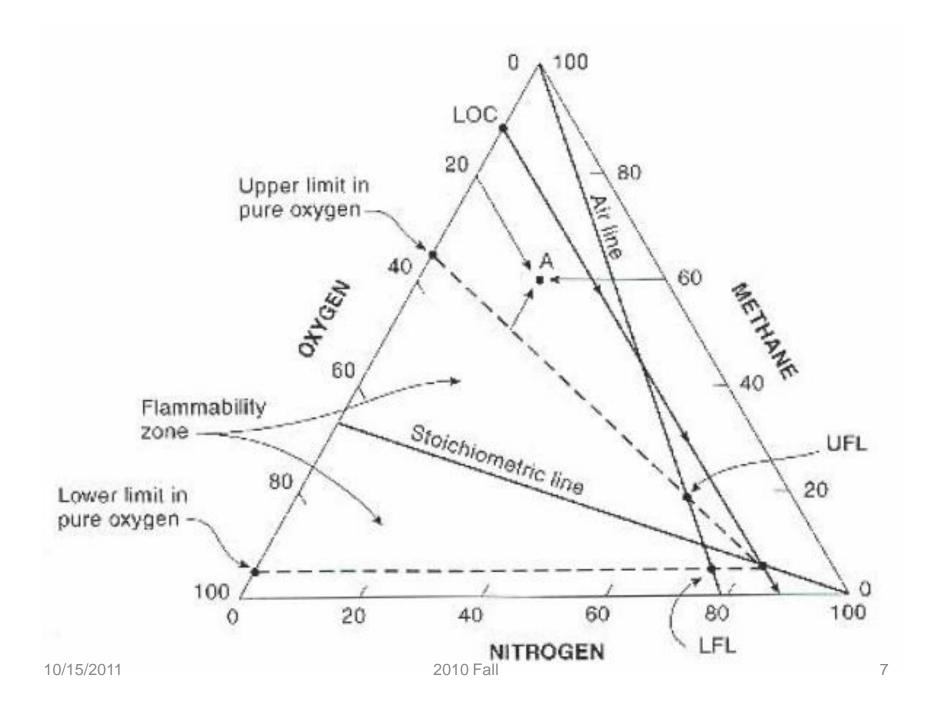
Estimate Flammability Limits

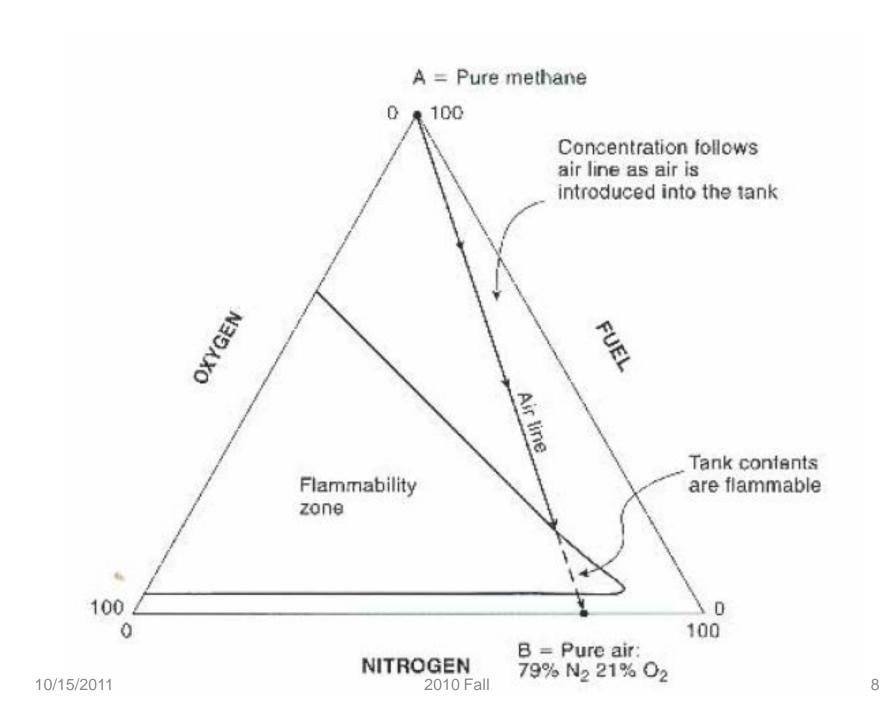
Combustion:
$$C_m H_x O_y + z O_2 \rightarrow mCO_2 + (x/2)H_2 O_2$$

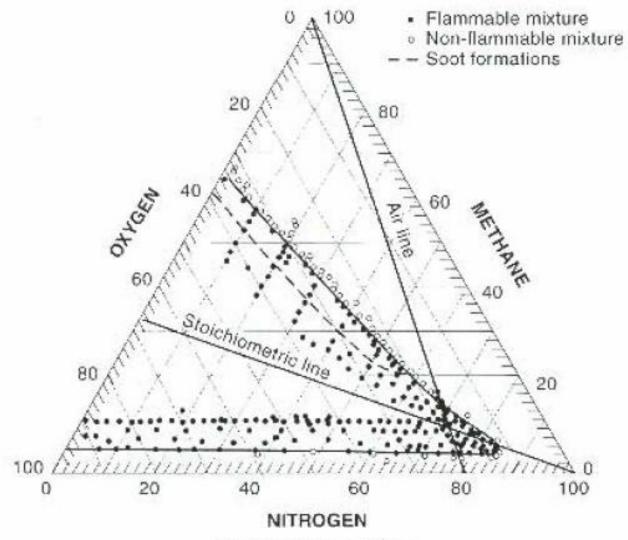
 $z, \frac{moles\ O_2}{moles\ fuel}, = m + x/4 - y/2$
 $C_{st} = \text{vol.}$ % fuel in air $= \frac{moles\ fuel}{moles\ fuel + moles\ air}$

$$= \frac{100}{1 + z/0.21} \quad \text{for 21 % O}_2 \text{ in air}$$

Jones correlation:
$$LFL = 0.55 C_{st}$$
; $UFL = 3.50 C_{st}$



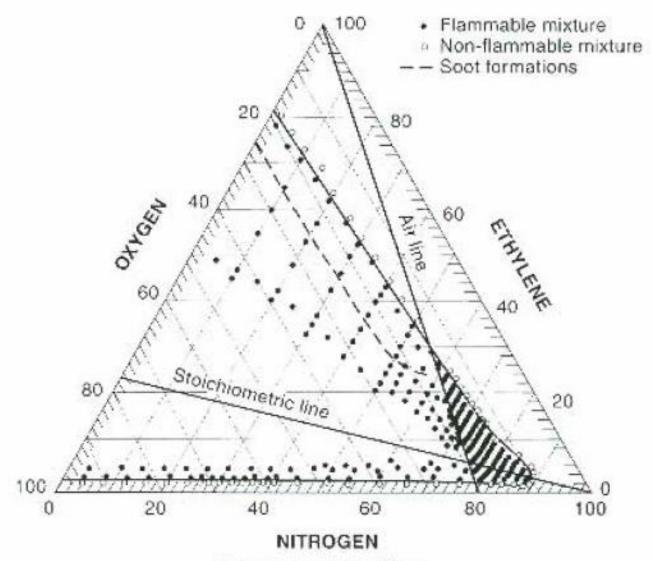




Experimental conditions

Initial pressure: 14.69 psia Initial temperature: 25°C Reactor volume: 20 liters Ignitor type: 1 cm 40 AWG SnCu / 500VA

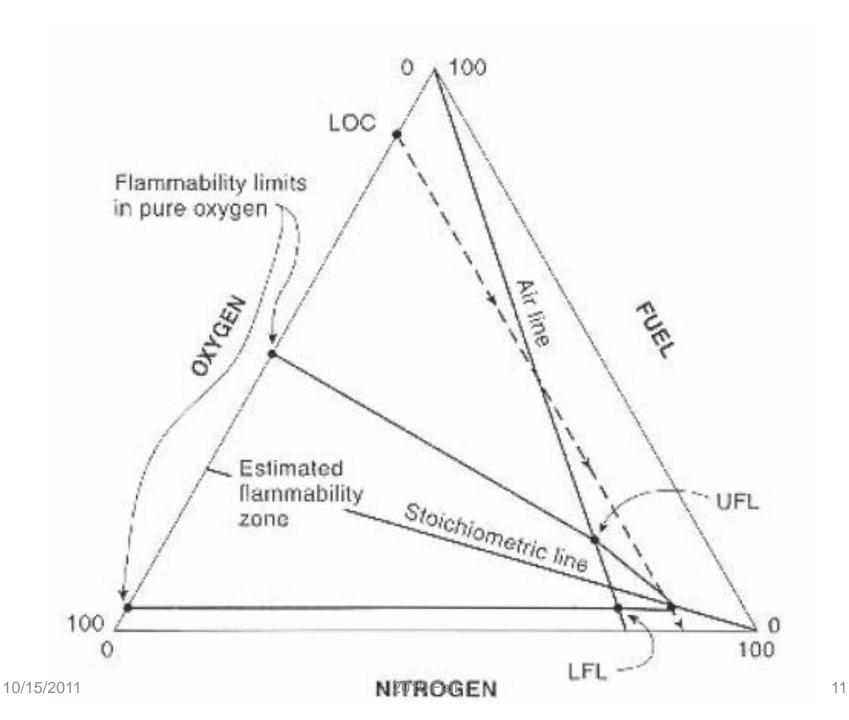
Ignitor energy: 10 J Ignitor location: Center 2010 Fall



Experimental conditions

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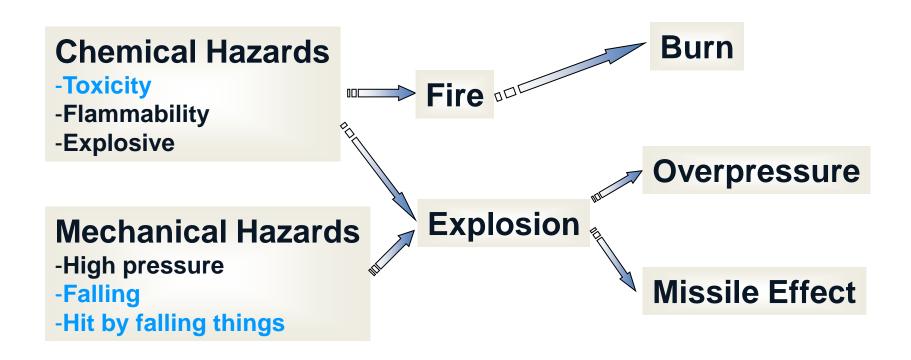
Limiting Oxygen Conc'n, LOC

- ♣ A minimum oxygen concentration (*LOC* or MOC) is required for combustion: Tab 6-2, p. 239.
- Inerting reduces oxygen below the minimum
- **4** Estimate *LOC* from stoichiometry and *LFL*:

$$LOC = \frac{O_2}{total} = \frac{fuel}{total} \frac{O_2}{fuel} = LFL \cdot z$$

P. 246, Fig. 6-10

Hazards to Fire & Explosion





Flammability Limit on T, P

Flammability on Temperature

$$LFL_{T} = LFL_{25} - \frac{0.75}{\Delta H_{c}} (T - 25)$$

$$UFL_{T} = UFL_{25} + \frac{0.75}{\Delta H_{c}}(T - 25)$$

Flammability on Pressure

$$UFL_P = UFL + 20.6(\log P + 1)$$



Too much is worse than too little (過猶不及) – Korean Old Saying

Minimum Ignition Energy (MIE)

- **MIE**: smallest energy to initiate combustion
- Each combustible material has a MIE.
- Decreases with increase in temperature
- Decreases with increase in pressure
- Increases with added inert materials
- Higher for dusts & aerosols than for gases
- Many HC gases have MIE ~ 0.25 mJ, Tab 6-4, p 248, compared to static discharges of ~ 25mJ

Table 6-4 Minimum Ignition Energy for Selected Gases¹

Chemical	Minimum ignition energy (mJ)	
Acetylene	0.020	
Benzene	0.225	
1,3-Butadiene	0.125	
n-Butane	0.260	
Cyclohexane	0.223	
Cyclopropane	0.180	
Ethane	0.240	
Ethene	0.124	
Ethylacetate	0.480	
Ethylene oxide	0.062	
n-Heptane	0.240	
Hexane	0.248	
Hydrogen	0.018	
Methane	0.280	
Methanol	0.140	
Methyl acetylene	0.120	
Methyl ethyl ketone	0.280	
n-Pentane	0.220	
2-Pentane	0.180	
Propane	0.250	

Autoignition Temperature, AIT

- **AIT**: temperature at which vapor ignites spontaneous from available energy
- **♣** *AIT* decreases with increases in P, V of material, or in O₂. App B, p. 566
- ♣ Auto-oxidation: oxidation is exothermic; energy can accumulate, increase T and oxidation rate → autoignition

Adiabatic Compression

- Rapid compression of a gas generates heat and increases temperature
- ♣ Over a short time process can be quasi adiabatic, where little heat is dissipated and T increases → exceed the AIT
- **Ex:** compressor, pre-ignition, O₂ systems

Ideal gas:
$$T_f = T_i \left(\frac{P_f}{P_i}\right)^{(\gamma-1)/\gamma}$$

Sources of Ignition

- Ignition sources include internal (autoignition) and external examples
- External sources usually numerous and difficult to eliminate. Tab 6-5, p 251
- Consider combustible in addition to "flammable" materials
- Employ other methods also, e.g., inerting, to avoid flammable ranges.

Table 6-5 Ignition Sources of Major Fires¹

Electrical (wiring of motors)	23%	
Smoking	18%	
Friction (bearings or broken parts)	10%	
Overheated materials (abnormally high temperatures)	8%	
Hot surfaces (heat from boilers, lamps, etc.)	7%	
Burner flames (improper use of torches, etc.)	7%	
Combustion sparks (sparks and embers)	5%	
Spontaneous ignition (rubbish, etc.)	4%	
Cutting and welding (sparks, arcs, heat, etc.)	4%	
Exposure (fires jumping into new areas)	3%	
Incendiarism (fires maliciously set)	3%	
Mechanical sparks (grinders, crushers, etc.)	2%	
Molten substances (hot spills)	2%	
Chemical action (processes not in control)	1%	
Static sparks (release of accumulated energy)	1%	
Lightning (where lightning rods are not used)	1%	
Miscellaneous	1%	
117.04		

¹Accident Prevention Manual for Industrial Operations (Chicago: National Safety Council, 1974).

Aerosols, Mists, Sprays

- ♣ Finely divided liquid drops of combustible materials in air + ignition source → explosion
- ♣ Flammability regions similar to gases but extend below flash point temp.
- **#** MIE values higher than for gases
- Droplets have higher r than gases
 - more energy and more damage if explode

Explosions

- Rapid reactions and energy releases
- Expansions of gases: pressure or shock wave (thermal & stoichiometric effects)
- Reaction front behind pressure or shock wave (abrupt pressure change)
- Damage due to energy dissipation effects, e.g., waves, projectiles, sound, radiation
- Most damage due to blast wave (pressure wave and wind)

Parameters significantly affecting the behavior of explosions

- **4** Ambient temperature
- **4** Ambient pressure
- Composition of explosive material
- Physical properties of explosive material
- Nature of ignition source:
 - type, energy, and duration
- **4** Geometry of surroundings:
 - confined or unconfined
- Amount of combustible material
- Turbulence of combustible material
- Time before ignition
- Rate at which combustible material is released

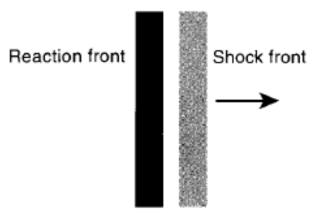
Detonations

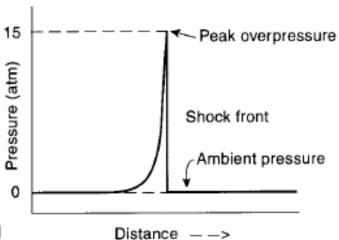
- Energy releases short, < 1 ms, and within small volume
- Shock and reaction front > speed of sound
- Mechanisms: thermal (self-accelerating and chain branching (free radicals)
- ♣ P of shock wave: ~ 10 100 atm.
- **♣** Damage: P_{max} , $(dP/dt)_{max}$, wind from explosion, duration of pressure wave

Deflagrations

- **♣** Energy release within ~ 0.3 s,
- Pressure front = speed of sound; reaction front behind at < speed of sound</p>
- Mechanism: turbulent diffusion, mass transfer limited
- ♣ P of wave: ~ a few atmospheres
- Can evolve, esp. in pipes, to a detonation due to adiabatic compression and heating
 - **⇒** pressure rise

DETONATION

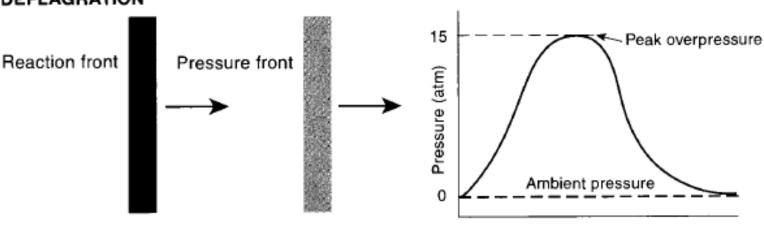




Distance -->

In a detonation, the reaction front moves at a speed greater than the speed of sound, driving the shock front immediately preceding it. Both fronts move at the same speed.

DEFLAGRATION



In a deflagration, the reaction front moves at a speed less than the speed of sound, while the pressure front moves away from the reaction front at the speed of sound.

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Safety Practices from Behavior

- Control concentrations outside combustion (flammability) range
- Dynamic behavior determined from experimental data



- \blacksquare Predict consequences: P_{max} , $(dP/dt)_{max}$
- **Robustness**, from $(dP/dt)_{max}$ to select pressure relief and timing for suppressants e.g., H₂O, CO₂, or Halon

2010 Fall

Robustness Data

Gases

Dusts

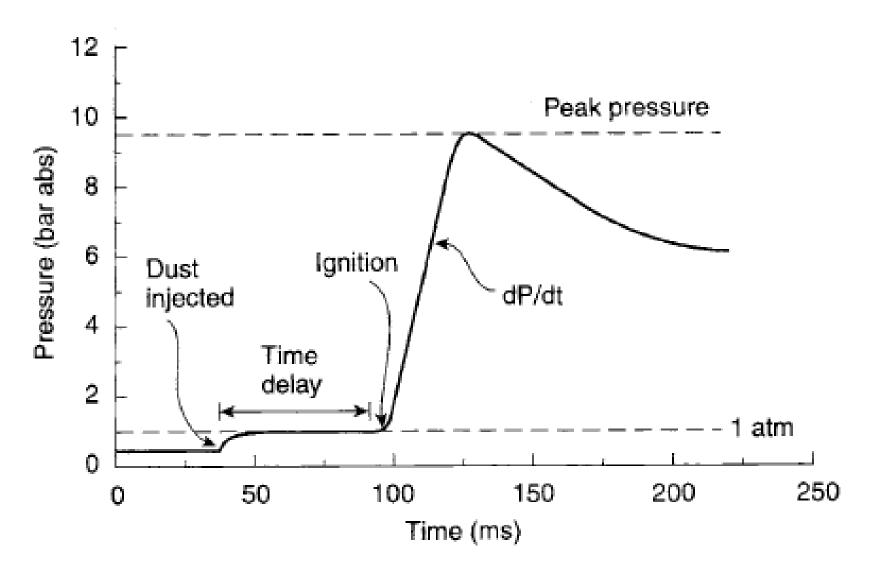
$$\left(\frac{dP}{dt}\right)_{\text{max}} V^{1/3} = K_G$$

$$\left(\frac{dP}{dt}\right)_{\text{max}} V^{1/3} = K_G \qquad \left(\frac{dP}{dt}\right)_{\text{max}} V^{1/3} = K_{St}$$

K_G, K_{St} are deflagration indices for gas, dust

$$\log\left(\frac{dP}{dt}\right)_{\text{max}} = \log K_G - (1/3)\log V$$

 $(dP/dt)_{max}$ smaller for larger V, Fig 6-19, p 259



Pressure data from dust explosion device

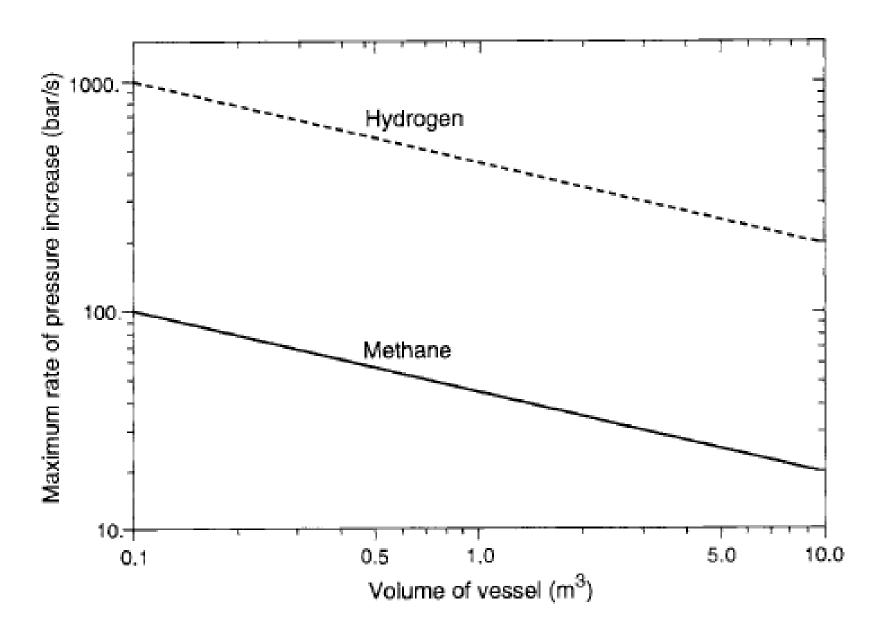


Table 6-8 St Classes for Dusts and Combustion Data for Dust Clouds¹

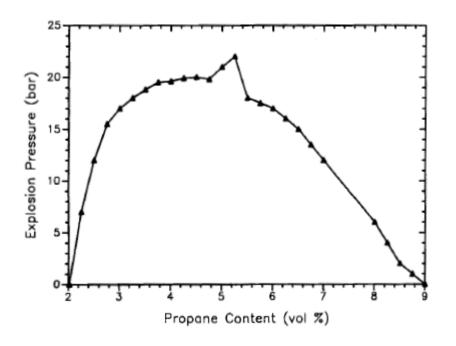
Deflagration index, K _{st} (bar m/s)	St class
0	St-0
1-200	St-1
200-300	St-2
>300	St-3

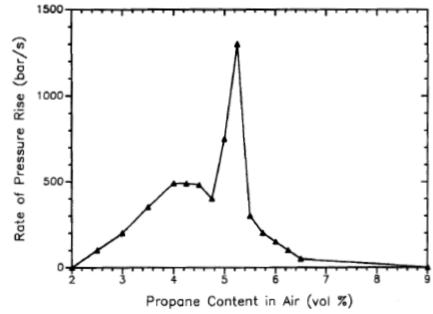
Dust	Median particle size (μm)	particle explosive dust size concentration		<i>K</i> _{St} (bar-m/s)	Minimum ignition energy (mJ)
Cotton, wood, peat	_				
Cotton	44	100	7.2	24	_
Cellulose	51	60	9.3	66	250
Wood dust	33	_	_	-	100
Wood dust	80	_	_		7
Paper dust	<10	_	5.7	18	_

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Effect of Pressure

- $+P_{max}$, $(dP/dt)_{max}$ are each proportional to initial pressure: Fig 6-20, p 263
- During a deflagration, increase in P can convert to a more damaging detonation, Fig 6-21, p 264
- ♣ Safety measures for pressures no higher than necessary: a) deflagrations are less damaging; b) detonations are less likely to occur





Dust Explosions

- ♣Finely divided combustible solids dispersed in air encounter an ignition source (complete the fire triangle)
- **♣**Dust explosion ⇒ disperse more dust
 - ⇒ subsequent explosion ⇒ continuation
- **4**Conditions for explosion:
 - #particles < certain size for ignition & propagation</pre>
 - **4**density in air from 20 g/m³ to 6 kg/m³ (*LEL*, *UEL*)
 - dispersion in air fairly uniform for propagation

Damage from Explosion

- Pressure wave and subsequent wind (blast wave)
- Reaction front, creating blast wave, ends when material consumed
- **♣** Peak overpressure, P_{max}
- Rate of pressure rise
- Duration of blast wave
- ♣ Damage estimates based on P_{max}, Tab 6-9, p. 267

Table 6-9 Damage Estimates for Common Structures Based on Overpressure (these values are approximations)¹

Pressure						
psig	kPa	Damage				
0.02	0.14	Annoying noise (137 dB if of low frequency, 10-15 Hz)				
0.03	0.21	Occasional breaking of large glass windows already under strain				
0.04	0.28	Loud noise (143 dB), sonic boom, glass failure				
0.1	0.69	Breakage of small windows under strain				
0.15	1.03	Typical pressure for glass breakage				
0.3	2.07	"Safe distance" (probability 0.95 of no serious damage below this value); projectile limit; some damage to house ceilings; 10% window glass broken				
0.4	2.76	Limited minor structural damage				
0.5-1.0	3.4-6.9	Large and small windows usually shatter; occasional damage to window frames				
0.7	4.8	Minor damage to house structures				
1.0	6.9	Partial demolition of houses, made uninhabitable				
1-2	6.9–13.8	Corrugated asbestos shatters; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panels (standard housing), fastenings fail, panels blow in				

1.3	9.0	Steel frame of clad building slightly distorted
2	13.8	Partial collapse of walls and roofs of houses
2-3	13.8 - 20.7	Concrete or cinder block walls, not reinforced, shatter
2.3	15.8	Lower limit of serious structural damage
2.5	17.2	50% destruction of brickwork of houses
3	20.7	Heavy machines (3000 lb) in industrial buildings suffer little damage;
		steel frame buildings distort and pull away from foundations
3-4	20.7-27.6	Frameless, self-framing steel panel buildings demolished; rupture of oil
		storage tanks
4	27.6	Cladding of light industrial buildings ruptures
5	34.5	Wooden utility poles snap; tall hydraulic presses (40,000 lb) in buildings
		slightly damaged
5-7	34.5-48.2	Nearly complete destruction of houses
7	48.2	Loaded train wagons overturned
7-8	48.2-55.1	Brick panels, 8-12 in thick, not reinforced, fail by shearing or flexure
9	62.0	Loaded train boxcars completely demolished
10	68.9	Probable total destruction of buildings; heavy machine tools (7000 lb)
		moved and badly damaged, very heavy machine tools (12,000 lb)
		survive
300	2068	Limit of crater lip

¹V. J. Clancey, "Diagnostic Features of Explosion Damage," paper presented at the Sixth International Meeting of Forensic Sciences (Edinburgh, 1972).

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Correlation for Overpressure

Convert energy of explosion, $m_c DH_c$, to an equivalent mass of TNT, m_{TNT}

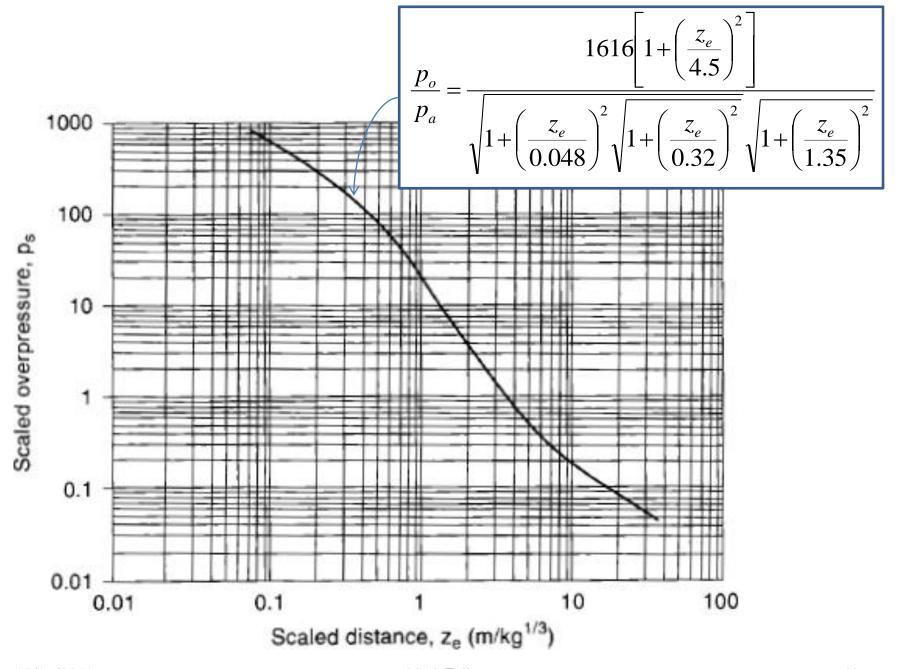
$$m_{TNT} = \frac{\eta m_c \Delta H_c}{1,120 \, cal/g}$$
 $\eta = \text{efficiency}$

Scaled distance:
$$z_e = \frac{r}{m_{TNT}^{1/3}}$$
 r = distance from explosion

Scaled overpressure: $p_s = p_o / p_a$

 p_o , peak overpressure (gauge); p_a , ambient pressure

Correlation for $p_s(z_e)$: Fig 6-23, p 268



Explosion Efficiency, η

- Incomplete mixing of material with air
- Incomplete conversion of thermal energy to mechanical energy
- Unconfined explosions: η often estimated within 1 10 %.
 - **↓** Use 2 % efficiency.
- ♣ Totally confined explosions, efficiency varies: assume 100 % efficiency of energy conversion ⇒ Ex 6-8, p 269

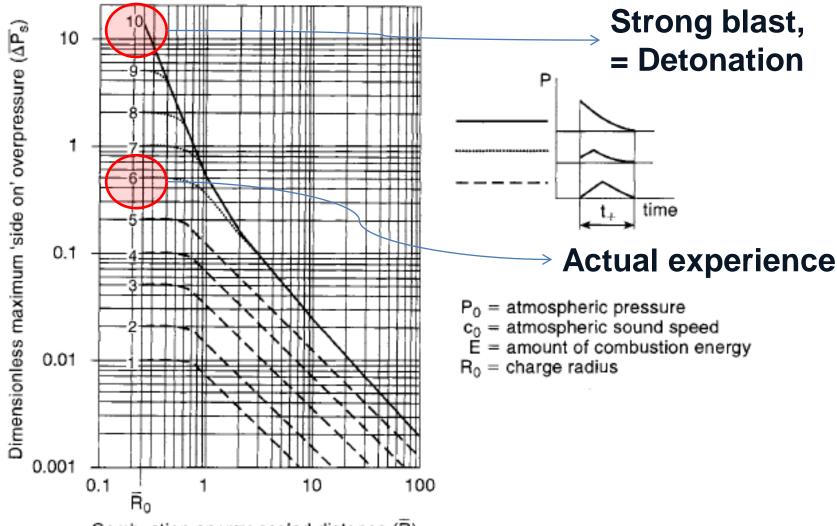
TNO Multi-Energy Method

With many experiments, empirical correlations suggested Sachs-scaled distance

$$\overline{R} = \frac{R}{(E/P_o)^{1/3}}$$

where \overline{R} the Sachs-scaled distance R the distance from the charge E the charge combustion energy P_o the ambient pressure

$$p_o = \Delta \overline{P}_S \cdot p_a$$



Combustion energy-scaled distance (R)

$$\Delta \overline{P}_s = \frac{\Delta P_s}{P_0}; \ \overline{t}_+ = \ \frac{t_+ c_0}{(E/P_0)^{1/3}}; \ \overline{R} = \ \frac{R}{(E/P_0)^{1/3}}$$

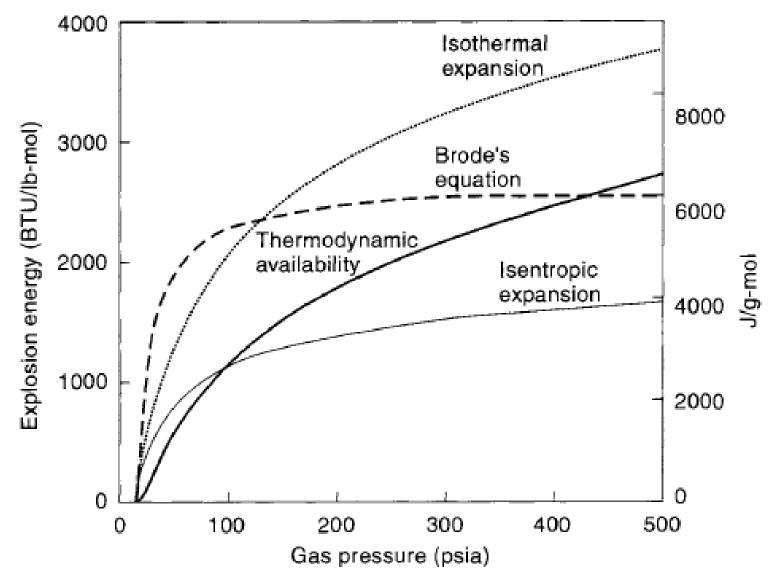
Chemical Explosion Energy

- Blast wave from expansion of gases
 - thermal energy heats reaction components
 - increase in # of moles (usually much smaller)
- Most of released energy converted to mechanical energy: Energy of explosion
- Energy of combustion: energy from complete combustion, larger and usually within about 10% of explosion energy.
- Energy values, App B, p 566

Mechanical Explosion Energy

- Various models to estimate energy released in a sudden expansion of gas: Fig 6-25, p 278
- Thermodynamic availability model, maximum mechanical energy obtainable from an expansion of gas into the atmosphere:

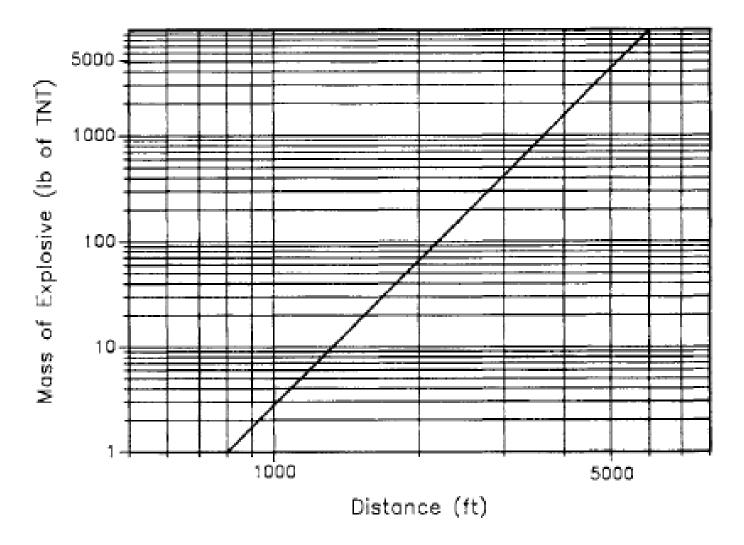
$$E_{\rm exp} = P_2 V \left| \ln \left(\frac{P_2}{P_1} \right) - \left(1 - \frac{P_1}{P_2} \right) \right|$$
 P_2 , release P_1 , ambient P_2



The energy of explosion for a compressed inert gas

Missile Energy Correlation

- Significant fraction of explosion energy often converted to kinetic energy of fragment, e.g., burst reactor vessel
- Clancey correlation of explosive mass (TNT equivalent) and range of fragments
- Propagation of explosion within a plant
- Estimate amount of mass involved in an explosion
- **♣** Fig 6-26, p 279



Maximum horizontal range of blast fragments

Explosion Damage to People

- Overpressure
- Thermal radiation
- Available overpressure data
- Probit correlation, Tab 2-5, p 51
 - Injuries from fragments
 - **4** Eardrum ruptures
 - Deaths and injuries from impact
 - Deaths from lung hemorrhage
 - Deaths from release of toxic chemicals

Table 2-4 Transformation from Percentages to Probits¹

%	0	1	2	3	4	5	6	7	8	9
0	10-	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

¹D. J. Finney, Probit Analysis, (Cambridge: Cambridge University Press, 1971), p. 25. Reprinted by permission.

Table 2-5 Probit Correlations for a Variety of Exposures (The causative variable is representative of the magnitude of the exposure.)

	Causative	Pro param		
Type of injury or damage	variable	K ₁	k ₂	
Fire ¹				_
Burn deaths from flash fire	$t_e I_e^{4/3}/10^4$	-14.9	2.56	
Burn deaths from pool burning	$tI^{4/3}/10^4$	-14.9	2.56	
Explosion ¹				
Deaths from lung hemorrhage	p^{o}	-77.1	6.91	
Eardrum ruptures	p^{o}	-15.6	1.93	
Deaths from impact	\overline{J}	-46.1	4.82	
Injuries from impact	J	-39.1	4.45	
Injuries from flying fragments	J	-27.1	4.26	
Structural damage	p^{o}	-23.8	2.92	
Glass breakage	p^{o}	-18.1	2.79	
Toxic release ²				
Ammonia deaths	$\sum C^{2.0}T$	-35.9	1.85	
Carbon monoxide deaths	$\Sigma C^{1.0}T$	-37.98	3.7	
Chlorine deaths	$\Sigma C^{2.0}T$	-8.29	0.92	
Ethylene oxide deaths ³	$\Sigma C^{1.0}T$	-6.19	1.0	
Hydrogen chloride deaths	$\Sigma C^{1.0}T$	-16.85	2.0	
Nitrogen dioxide deaths	$\sum C^{2.0}T$	-13.79	1.4	
Phosgene deaths	$\sum C^{1.0}T$	-19.27	3.69	
Propylene oxide deaths	$\Sigma C^{2.0}T$	-7.42	0.51	
Sulfur dioxide deaths	$\sum C^{1.0}T$	-15.67	1.0	
Toluene	$\Sigma C^{2.5}T$	-6.79	0.41	

Vapor Cloud Explosions (VCE)

- Potential for VCE: processes with liquefied gases, superheated liquids, high pressure gases with the release of flammable gases
- Stages:
 - a) Reactor ruptures
 - b) Pressurized liquid releases flammable vapor
 - c) Vapor disperses and mixes with air
 - d) Vapor encounters ignition source and exploded



VCE Accidents (1)

4 Flixborough, England, 1974

- A sudden failure of a 20-inch cyclohexane line between reactors led to vaporization of an estimated 30 tons of cyclohexane.
- The vapor cloud dispersed throughout the plant site
- Ignited by an unknown source 45 seconds after the release.
- The entire plant site was demolished and 28 people were killed
- **429 VCEs the period 1974-1986**
 - Property losses \$5,000,000 ~ \$100,000,000
 - 140 fatalities



VCE Accidents (2)

VCEs increased

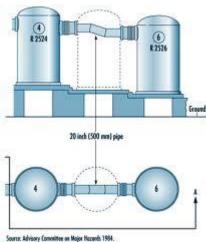
- Increase in inventories of flammable materials in process plants
- Operations at more severe conditions.
- Any process containing quantities of liquefied gases, volatile superheated liquid, or high-pressure gases is considered a good candidate for a VCE.
- **VCEs** are difficult to characterize
 - **Large number of parameters to describe an event.**
 - **Accidents occur under uncontrolled circumstances.**
 - ♣ Data collected from real events are mostly unreliable and difficult to compare.

VCE Accidents (3)

- VCE parameters
 - Quantity of material released,
 - Fraction of material vaporized,
 - Probability of ignition of the cloud,
 - Distance traveled by the cloud before ignition,
 - Time delay before ignition of cloud
 - Probability of explosion rather than fire
 - Existence of a threshold quantity of material
 - Efficiency of explosion
 - Location of ignition source with respect to release.







Safety Practices to Prevent VCE

- Safety focuses on prevention. Cannot control a large cloud of released flammable material.
- Inherent safety: minimize and moderate
 - minimum amounts of volatile flammables
 - process conditions that minimize flashing
 - leak detectors
 - automated shutoff valves to limit releases

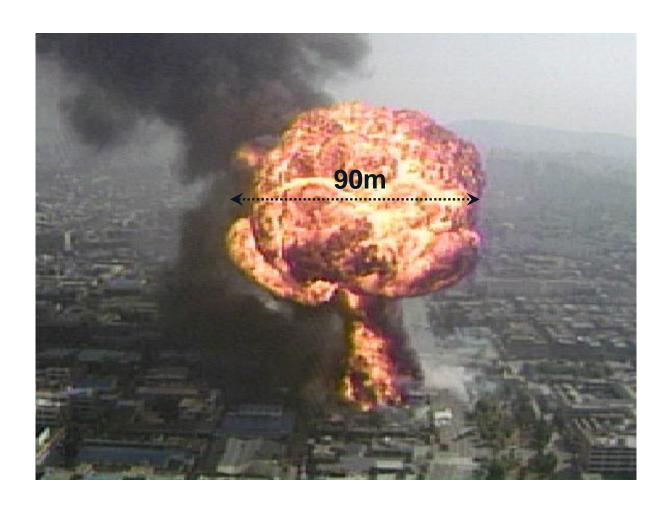
Boiling-Liquid Expanding-Vapor Explosions (*BLEVE*)

- **BLEVE**: Explosive vaporization of a liquid at a temperature above its normal boiling point caused by container rupture.
 - Ex: from external fire
- **♣** If liquid is flammable, a *VCE* can result
- Boiling liquid can propel vessel fragments
- **4** Fraction of liquid vaporized, $T_o > T_b$:

$$f_V = \frac{m_V}{m_L} = \frac{C_p(T_o - T_b)}{\Delta H_V}$$

BLEVE Procedure

- 1. A fire develops adjacent to a tank containing a liquid.
- 2. The fire heats the walls of the tank.
- 3. The tank walls below liquid level are cooled by the liquid, increasing the liquid temperature and the pressure in the tank.
- 4. If the flames reach the tank walls or roof where there is only vapor and no liquid to remove the heat, the tank metal temperature rises until the tank loses it structural strength.
- 5. The tank ruptures, explosively vaporizing its contents



BLEVE at butane tank lorry

The duration and diameter of fireball are

$$t_{BLEVE} = 0.825 M_{fireball}^{0.26}$$

$$D_{\text{max}} = 6.48 M_{\text{fireball}}^{0.325}$$

With fireball of butane, T = 7 sec and D = 90 m(ca. 3.7 ton involved)

Home assignment Crowl, 6-3, 6, 12, 24, 29